COPOLYMER COMPOSITION

A Chapter in

Comprehensive Polymer Science

by

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The successful synthesis of new materials via free radical copolymerization requires a thorough understanding of the factors that control the structures of copolymer chains. Of the primary structural variables used to describe polymer chains, two (copolymer composition and comonomer sequence distribution) are unique to copolymers. The present chapter examines the compositions and sequences of copolymers prepared via free-radical processes.

The products of free radical copolymerizations are, with few exceptions, determined by the kinetics, rather than the thermodynamics, of the chain growth process. The problem of predicting copolymer composition and sequence then reduces to the writing of a set of differential equations that describe the rates at which each of the two monomers enters the copolymer chain by attack of the growing macroradical. This requires a kinetic model of the copolymerization process, and several such models have been described in the copolymerization literature. The following sections examine the fundamental bases of the most important of these models, and assess the degree to which such models can account for experimentally observed copolymerization behavior.

TERMINAL MODEL

Theory. The standard kinetic treatment of free radical copolymerization was introduced in 1944, in papers contibuted independently by Mayo and Lewis,[1] by Alfrey and Goldfinger[2] and by Wall.[3] Following earlier suggestions by Dostal,[4] by Norrish and Brookman,[5] and by Jenckel,[6] Mayo and Lewis described their experimental work on the radical copolymerization of styrene and methyl methacrylate in terms of a model in which the rate constant for addition of each monomer was assumed to be dependent on the identity of the terminal unit on the growing chain. Four elementary propagation steps were then considered (Eqns 1-4):

$$\sim\sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim\sim M_1M_1\bullet \quad (1)$$

$$\sim\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim\sim M_1M_2\bullet \quad (2)$$

$$\sim\sim M_2\bullet + M_1 \xrightarrow{k_{21}} \sim\sim M_2M_1\bullet \quad (3)$$

$$\sim\sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim\sim M_2M_2\bullet \quad (4)$$

By writing differential equations that describe the rates of disappearance of monomers M_1 and M2, and by assuming steady-state concentrations of the radical centers $M_1\bullet$ and $M_2\bullet$, one arrives at a simple expression that relates the ratio of monomers in the copolymer ($d[M_1]/d[M_2]$) to the concentrations of monomers in the feed mixture ($[M_1]$ and $[M_2]$) (Eqn 5):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \qquad (5)$$

The parameters r_1 and r_2 are ***reactivity ratios*** defined as:

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21} \qquad (6)$$

A detailed derivation of Eqn 5 is given in Ch. 2 of this volume. (EDITOR: This is intended to refer the reader to Prof. Harnielec's chapter.)

Analysis of the terminal model is readily extended to the prediction of copolymer sequence distribution. Sequence distributions are most generally and conveniently specified in terms of the number fractions of uninterrupted sequences of a given monomer (M_1 or M2) that are of a particular length. The number fraction is of course identical to the probability that a given uninterrupted sequence, selected at random, is of that length. Consider a sequence of M_1 units of length x. Such a sequence arises in the terminal model when a growing macroradical terminating in $M_1\bullet$ adds (x - 1) M_1's followed by an M2. The probability that such a sequence forms is obtained as the product of the probabilities of each of the independent steps that lead to the sequence. Thus the number fraction of sequences of M_1 of length x (N_x^1) is given as:

$$N_x^1 = P_{11}^{(x-1)} P_{12} \qquad (7)$$

where P_{11} is the probability that $\sim\sim M_1\bullet$ adds M_1:

$$P_{11} = \frac{k_{11}[M_1\bullet][M_1]}{k_{11}[M_1\bullet][M_1] + k_{12}[M_1\bullet][M_2]} = \frac{r_1}{r_1 + [M_2]/[M_1]} \qquad (8)$$

and P_{12} (= 1 - P_{11}) is the probability that $\sim\sim M_1\bullet$ adds M2. The lengths of M_2 sequences are determined in similar fashion, such that:

$$N_x^2 = P_{22}^{(x-1)} P_{21} = \frac{r_2}{r_2 + [M_1]/[M_2]} \qquad (9)$$

Thus Eqns 8 and 9 allow calculation of the comonomer sequence distribution from a knowledge of the terminal model reactivity ratios and the monomer feed composition. Use of Eqns 5, 8 and 9 is of course restricted to conditions under which the monomer feed composition is fixed. In practical terms, this requires the use of low monomer conversions in order to avoid serious errors arising from compositional drift as M_1 and M_2 enter the copolymer chain at different rates. Use of the integrated form of Eqn 5 has been recommended in order to relax the low-conversion restriction (cf. Ch. 2 of this volume) (EDITOR: Refer to Hamielec chapter.)

Experiment. The terminal model has proven remarkably successful in correlating a large body of copolymerization data. Greenley[7] has provided the most recent tabulation of free-radical reactivity ratios, in which some 900 ratios were recalculated, via the equations of Kelen and Tudos,[8,9] from the original experimental data. Table I lists some representative reactivity ratios for several of the most important vinyl monomers.

TABLE I HERE

The data in Table I provide several important insights regarding the current status of our understanding of radical copolymerization. First, the observed reactivity patterns may be divided into a rather small number of classes, which may be distinguished from one another on the basis of the magnitudes of r_1 and r_2. The most useful classification is as follows.

$r_1 \approx r_2 \approx 1$ ($k_{11} = k_{12}$; $k_{21} = k_{22}$): Neither radical center shows substantial preference for either M_1 or M2, so that the relative rates of monomer consumption are determined only by the relative monomer concentrations in the feed mixture. Eqn 5 simplifies to:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \qquad (10)$$

and the copolymer and monomer feed compositions are thus identical. Of the copolymerization systems listed in Table I, butadiene-styrene (r_1 = 1.35-1.83; r_2 = 0.37-0.84) and vinyl acetate-vinyl chloride (r_1 = 0.24-0.98; r_2 = 1.03-2.30) approach this pattern most closely. Each shows

small but significant deviations, however, so that compositional drift with conversion becomes an important practical concern.

$r_1 \approx r_2 \approx 0$ ($k_{11} = k_{22} = 0$): Each of the radical centers shows a strong preference for cross-propagation. In the extreme case, the copolymer is perfectly alternating and of 1:1 composition, regardless of the composition of the monomer feed mixture. Eqn 5 simplifies to:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{[M_2]}{[M_1]} = 1 \qquad (11)$$

The copolymerization of maleic anhydride ($r_1 = 0.00\text{-}0.02$) with styrene ($r_2 = 0.00\text{-}0.097$) behaves in this manner.

$r_1 > 1$; $r_2 < 1$ ($k_{11} > k_{12}$; $k_{21} > k_{22}$): Each of the radical centers prefers to add M_1, so that the copolymer is always enriched in M_1 relative to the feed. This situation arises frequently in radical copolymerization, and many examples may be found in Table I. A special case is that in which $r_1 r_2 = 1$ ($k_{11}/k_{12} = k_{21}/k_{22}$); i.e., in which both active centers show the same preference for addition of one of the monomers. Eqn 5 then becomes:

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \qquad (12)$$

This behavior is often termed ideal copolymerization.

$r_1 < 1$; $r_2 < 1$ ($k_{12} > k_{11}$, $k_{21} > k_{22}$): Each of the radical centers prefers cross-propagation, but the preference is not absolute. This results in a tendency toward alternation, which grows stronger as r_1 and r_2 approach zero. The copolymerization of acrylonitrile ($r_1 = 0.00\text{-}0.17$) with styrene ($r_2 = 0.29\text{-}0.55$) provides a good example. A characteristic of such copolymerizations is the existence of the so-called azeotropic composition, at which the copolymer and feed compositions are equal. This situation arises when:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \qquad (13)$$

which requires that:

$$\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} = 1 \qquad (14)$$

so that:

$$\frac{[M_1]}{[M_2]} = \frac{1 - r_2}{1 - r_1} \qquad (15)$$

at the azeotropic point. The azeotropic composition is of some practical significance in that at this point compositional drift with conversion may be neglected. This allows batch copolymerizations to be run to high conversions without the introduction of substantial compositional heterogeneity into the product (cf. Ch. 2; EDITOR: Refer to Hamielec).

The patterns of copolymerization behavior discussed above are summarized most succinctly in the form of composition curves in which copolymer composition (e.g., as mole fraction M_1 in the copolymer) is plotted as a function of the monomer feed composition (as mole fraction M_1 in the feed). Figure 1 shows schematic composition curves for each of the four classes of copolymerizations described above. Such composition curves, calculated via Eqn 5, reproduce in satisfactory fashion the experimental compositions obtained in the vast majority of radical copolymerizations. Thus the terminal model is extraordinarily useful as a context in which to describe the compositions of copolymers prepared from vinyl monomers of widely varying structure and reactivity. On the other hand, the model is not as successful in the prediction of comonomer sequence distribution[114] and overall copolymerization rate.[115]

A second point that becomes apparent on examination of Table I is that the experimentally reported reactivity ratios, even for these most common vinyl monomers, span some range. It is not at all uncommon for the highest and lowest reported values to differ by a factor of 2 for a given copolymerization, and much larger variation may be found. The sources of experimental and statistical uncertainty in determining reactivity ratios are discussed in Ch. 2. (EDITOR: Refer to Hamielec.)

PENULTIMATE MODEL

The fundamental assumption of the terminal model, i.e., that the reactivity of the growing radical is determined only by the identity of the last-added monomer unit, is equivalent to the assumption that the relative rates of monomer addition are insensitive to substitution at positions more remote than that β to the radical center. Remote substituent effects are well known in organic chemistry, and it is plausible that copolymerization reactivity ratios should be affected by units that precede the terminal residue on the propagating macroradical. Merz, Alfrey and Goldfinger[116] suggested in 1946 that a proper description of the propagation step should take into account four distinct active centers, which are defined by the identities of their terminal and penultimate units:

$$\sim\sim M_1M_1\bullet + M_1 \xrightarrow{k_{111}} \sim\sim M_1M_1M_1\bullet \quad (16)$$

$$\sim\sim M_1M_1\bullet + M_2 \xrightarrow{k_{112}} \sim\sim M_1M_1M_2\bullet \quad (17)$$

$$\sim\sim M_2M_1\bullet + M_1 \xrightarrow{k_{211}} \sim\sim M_2M_1M_1\bullet \quad (18)$$

$$\sim\sim M_2M_1\bullet + M_2 \xrightarrow{k_{212}} \sim\sim M_2M_1M_2\bullet \quad (19)$$

$$\sim\sim M_1M_2\bullet + M_1 \xrightarrow{k_{121}} \sim\sim M_1M_2M_1\bullet \quad (20)$$

$$\sim\sim M_1M_2\bullet + M_2 \xrightarrow{k_{122}} \sim\sim M_1M_2M_2\bullet \quad (21)$$

$$\sim\sim M_2M_2\bullet + M_1 \xrightarrow{k_{221}} \sim\sim M_2M_2M_1\bullet \quad (22)$$

$$\sim\sim M_2M_2\bullet + M_2 \xrightarrow{k_{222}} \sim\sim M_2M_2M_2\bullet \quad (23)$$

The copolymer composition is determined by the relative rates of monomer consumption:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{111}[M_1M_1\bullet][M_1] + k_{211}[M_2M_1\bullet][M_1] + k_{121}[M_1M_2\bullet][M_1] + k_{221}[M_2M_2\bullet][M_1]}{k_{112}[M_1M_1\bullet][M_2] + k_{212}[M_2M_1\bullet][M_2] + k_{122}[M_1M_2\bullet][M_2] + k_{222}[M_2M_2\bullet][M_2]} \quad (24)$$

Assumption of steady-state concentrations of each of the four radical centers leads to Eqn 25 for the copolymer composition:

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + \dfrac{r_{21}X(r_{11}X + 1)}{r_{21}X + 1}}{1 + \dfrac{r_{12}(r_{22} + X)}{X(r_{12} + X)}} \qquad (25)$$

where $X = [M_1]/[M_2]$ and the reactivity ratios are defined as:

$$r_{11} = \frac{k_{111}}{k_{112}} \qquad r_{21} = \frac{k_{211}}{k_{212}} \qquad r_{12} = \frac{k_{122}}{k_{121}} \qquad r_{22} = \frac{k_{222}}{k_{221}} \qquad (26)$$

Prediction of monomer sequence lengths by the penultimate model is conceptually identical to that described previously for the terminal model. The probability (P_{211}) that an $\sim\sim M_2M_1\bullet$ chain end adds M_1 is:

$$P_{211} = \frac{k_{211}[M_2M_1\bullet][M_1]}{k_{211}[M_2M_1\bullet]Mil + k_{212}[M_2M_1\bullet][M_2]} - \frac{[M_1]}{[M_1] + [M_2]/r_{21}} \qquad (27)$$

and:

$$P_{111} = \frac{[M_1]}{[M_1] + [M_2]/r_{11}} \qquad (28)$$

A sequence consisting of an isolated M_1 unit arises only when an $\sim\sim M_2M_1\bullet$ chain end adds M2, so the number fraction of M_1 sequences that are of length 1 is:

$$N_1{}^1 = 1 - P_{211} \qquad (29)$$

For longer sequences, enumeration of the required propagation steps leads to:

$$N_x{}^1 = P_{211}\,P_{111}{}^{(x-2)}\,(1 - P_{111}) \qquad (30)$$

Eqns 25, 29 and 30 for the penultimate model are thus equivalent to Eqns 5 and 8 developed previously for the terminal model; in each case, knowledge of the copolymerization reactivity ratios allows calculation of copolymer compositions and sequences as functions of the ratio of monomer concentrations in the feed.

COMPLEX PARTICIPATION MODEL

Radical copolymerizations of electron-rich olefins with electron-poor olefins are anomalous in several respects. Such monomer pairs often afford alternating copolymers over the entire range

of feed compositions,[117] and one often observes in such systems a marked sensitivity of the overall copolymerization rate to temperature, solvent and monomer concentration.[118,119] Butler and coworkers have also noted anomalies in the stereochemistry[120-122] and regiochemistry[123] of certain copolymerizations of electron-rich and electron-poor olefins.

A mechanistic scheme that accounts for this behavior invokes the participation of 1:1 olefinic electron donor-acceptor (EDA) complexes in the propagation step. Specifically, it is proposed that the 1:1 complex ($\overline{M_1M_2}$) competes with free monomers for the growing chain end. Modification of the terminal model in this way requires consideration of eight propagation steps:

$$\sim\sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim\sim M_1M_1\bullet \quad (31)$$

$$\sim\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim\sim M_1M_2\bullet \quad (32)$$

$$\sim\sim M_2\bullet + M_1 \xrightarrow{k_{21}} \sim\sim M_2M_1\bullet \quad (33)$$

$$\sim\sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim\sim M_2M_2\bullet \quad (34)$$

$$\sim\sim M_1\bullet + \overline{M_1M_2} \xrightarrow{k_{112}} \sim\sim M_1M_1M_2\bullet \quad (35)$$

$$\sim\sim M_1\bullet + \overline{M_2M_1} \xrightarrow{k_{121}} \sim\sim M_1M_2M_1\bullet \quad (36)$$

$$\sim\sim M_2\bullet + \overline{M_1M_2} \xrightarrow{k_{212}} \sim\sim M_2M_1M_2\bullet \quad (37)$$

$$\sim\sim M_2\bullet + \overline{M_2M_1} \xrightarrow{k_{221}} \sim\sim M_2M_2M_1\bullet \quad (38)$$

if radical additions to each "side" of the complex are regarded as distinct, and a complexation equilibrium:

$$M_1 + M_2 \overset{K}{\rightleftharpoons} \overline{M_1M_2} \quad (39)$$

An analysis of this model, which predicts copolymer composition and sequence as functions of the feed composition, has been provided by Hill and coworkers.[124] The mole ratio of M_1 to M_2 in the copolymer is given as:

$$\frac{d[M_1]}{d[M_2]} = \frac{(1 - P_{22})(P_{12} + P_{1\bar{1}2}) + (1 - P_{12})(P_{21} + P_{2\bar{2}\bar{1}})}{(1 - P_{21})(P_{12} + P_{1\bar{1}2}) + (1 - P_{11})(P_{21} + P_{2\bar{2}\bar{1}})} \quad (40)$$

where the transition probabilities are defined as:

$$\begin{aligned} p22 &= r_2[M_2]/\Sigma M_2 & P_{21} &= [M_1]/\Sigma M_2 \\ P_{212} &= s_2[\overrightarrow{M_1M_2}]/\Sigma M_2 & P_{221} &= s_2q_2[\overline{M_1M_2}]/\Sigma M_2 \\ P_{12} &= [M_1]/\Sigma M_1 & P_{11} &= r_1[M_1]/\Sigma M_1 \\ P_{112} &= s_1q_1[\overline{M_1M_2}]/\Sigma M_1 & P_{121} &= s_1[\overrightarrow{M_1M_2}]/\Sigma M_1 \end{aligned} \quad (41)$$

with

$$\Sigma M_1 = [M_1] + r_1[M_1] + s_1[\overrightarrow{M_1M_2}][1 + q_1] \quad (42)$$

and

$$\Sigma M_2 = r_2[M_2] + [M_1] + s_2[\overrightarrow{M_1M_2}][1 + q_2] \quad (43)$$

The reactivity ratios in this formulation are defined as:

$$r_1 = k_{11}/k_{12} \qquad r_2 = k_{22}/k_{21} \quad (44)$$

$$q_1 = k_{1\bar{1}2}/k_{1\bar{2}\bar{1}} \qquad 92 = k_{2\bar{2}\bar{1}}/k_{2\bar{1}\bar{2}} \quad (45)$$

$$s_1 = k_{1\bar{2}\bar{1}}/k_{12} \qquad s_2 = k_{2\bar{1}\bar{2}}/k_{21} \quad (46)$$

so that Eqn 40 specifies the copolymer composition in terms of monomer concentrations and seven parameters (six reactivity ratios and the complexation equilibrium constant, K).

Sequence information can be calculated in the usual manner, i.e., as the number fraction of sequences of either monomer of length x. For M_1, the number fraction of sequences of length x is:

$$N_1^x = \frac{p_1^x}{\sum_{m=1}^{\infty} p_1^m} \quad (47)$$

where

$$p_1^1 = P_2 \frac{[(1 - P_{11})(P_{12} + P_{12\bar{1}})(P_{21} + P_{2\bar{2}\bar{1}}) + P_{2\bar{1}\bar{2}}(P_{1\bar{1}2} + P_{12})]}{(P_{1\bar{1}2} + P_{12})} \quad (48)$$

and

$$p_1^x = P_2 P_{11}^{(x-2)} \frac{[(1 - P_{11})(P_{21} + P_{22\bar{1}})(P_{12}P_{11} + P_{12\bar{1}}P_{11} + P_{1\bar{1}\bar{2}})}{(P_{1\bar{1}\bar{2}} + P_{12})} \quad (49)$$

The quantity P_2 is the probability of selecting an M_2 unit that entered the chain either as free M_2 or via the reactions shown in Eqns 35 and 37. However, P_2 need not be evaluated, since this quantity may be eliminated from the expression (Eqn 47) for N_x^1. Eqns 40 and 47 thus allow calculation of copolymer composition and sequence as functions of the monomer feed composition.

OTHER COPOLYMERIZATION MODELS

The terminal, penultimate and complex participation models have been discussed widely in the copolymerization literature. Two additional models - the complex dissociation model and the depropagation model - have not been considered as extensively, but each is physically plausible and each has been analyzed in sufficient detail that compositions and sequences may be calculated. These models are outlined briefly here; the reader is directed to the original papers for a thorough description.

Complex Dissociation Model. Tsuchida and Tomono[125] suggested in 1971 that EDA complexes may take part in radical copolymerizations not by adding to the chain end in a concerted fashion, but rather by delivering only one of the two complexed monomers. Thus the terminal model must be modified by consideration of four new propagation steps:.

$$\sim\sim M_1\bullet + \overline{M_1M_2} \longrightarrow \sim\sim M_1M_1\bullet + M_2 \quad (50)$$

$$\sim\sim M_1\bullet + \overline{M_1M_2} \longrightarrow \sim\sim M_1M_2\bullet + M_1 \quad (51)$$

$$\sim\sim M_2\bullet + \overline{M_1M_2} \longrightarrow \sim\sim M_2M_1\bullet + M_2 \quad (52)$$

$$\sim\sim M_2\bullet + \overline{M_1M_2} \longrightarrow \sim\sim M_2M_2\bullet + M_1 \quad (53)$$

Hill and coworkers[126] have provided an analysis of this kinetic scheme, and have demonstrated the calculation of copolymer composition and sequence according to this model.

Copolymerization with Depropagation. Most radical copolymerizations are strongly exothermic and effectively irreversible. Near the ceiling temperature, however, the influence of depropagation must be considered. Lowry[127] in 1960 developed a general theory that predicts copolymer composition for systems in which the addition of one of the two monomers is reversible. O'Driscoll and coworkers[128] subsequently derived composition equations equivalent to but more general than those of Lowry, and provided expressions for sequence distributions as well.

EVALUATION OF COPOLYMERIZATION MODELS

Three experimental approaches have been used to evaluate the theoretical treatments of copolymerization discussed above. The majority of such studies have compared measured compositions and sequences with those predicted by each of the kinetic models. But in fact, the determination of sequence distributions is still a considerable technical challenge, so that many investigators have been limited to composition measurements alone. More recently, measurements of absolute rate constants and trapping experiments on simple model radicals have been brought to bear on questions of copolymerization mechanism.

Composition and Sequence. It was recognized early in the study of radical copolymerization that sequence distribution should be more sensitive than composition to the details of the chain growth process. In their original paper on the penultimate model,[116] Merz, Alfrey and Goldfinger pointed out that it is not in measurements of composition, but rather "in the length of the [comonomer] sequences that the effect of the monomer in the chain preceding the free-radical chain end would become noticeable..." Berger and Kuntz[129] in 1964 analyzed this problem quantitatively for several hypothetical and several real copolymerizations. They showed, for example, that the compositions predicted by the terminal and penultimate models would be indistinguishable over a 1000-fold variation in $[M_1]/[M_2]$, for a system in which the terminal model reactivity ratios are $r_1 = 0.1$ and $r_2 = 0.9$ and the penultimate model parameters are $r_{11} = 0.94$, $r_{21} = 0.01$, $r_{22} = 0.9$ and $r_{12} = 5$. Thus quite large penultimate effects ($r_{11}/r_{21} = 94$) can be masked. On the other hand, much more modest effects are readily apparent in the predicted

sequence distributions. Analysis of the copolymerization of styrene (M_1) and maleic anhydride (M_2) according to the terminal ($r_1 = 0.0227$, $r_2 = 0$) or penultimate ($r_{11} = 0.017$, $r_{21} = 0.063$, $r_{12} = r_{22} = 0$) models leads to rather different predictions. In the terminal model analysis, the number fraction of styrene residues isolated between maleic anhydride units is 0.23; in the penultimate model analysis, 0.09. Thus a penultimate effect of a factor of five leads to sequence predictions markedly different from those of the terminal model.

More recently, Hill and coworkers have analyzed the bulk copolymerization of styrene and acrylonitrile in terms of the composition and sequence predictions of the terminal, penultimate and complex participation models.[114] They find that all three models reproduce the experimental composition data rather well, although the penultimate and complex models offer statistically significant improvements over the terminal model. Figure 2 shows the experimental compositions as well as the best-fit predictions of each of the three models. The predictions are remarkably similar, and data of very high precision are required for model discrimination. The sequence predictions of the three models are quite different, however, and allow a clear distinction between the penultimate and complex kinetic schemes (Figure 3). Hill and coworkers conclude that the bulk copolymerization of styrene and acrylonitrile is best described by a penultimate model with $r_{SS} = 0.23$, $r_{AS} = 0.63$, $r_{SA} = 0.09$ and $r_{AA} = 0.04$.

Determination of copolymer sequence has also provided insight into the effects of solvent on radical copolymerization. Harwood and coworkers have noted that copolymerizations that involve ionic, highly polar or hydrogen-bonding monomers are subject to large solvent effects; (i.e., the composition curves for such copolymerizations vary dramatically with solvent).[130] Furthermore, sequence distributions determined in such systems are inconsistent with the predictions of any of the conventional kinetic schemes, if one uses reactivity ratios determined from the relation between copolymer composition and monomer feed composition. On the other hand, comparison of the sequence distributions of copolymers of identical composition (but prepared in different solvents from feeds of different $[M_1]/[M_2]$) shows them to be identical. Harwood concludes that the conditional probabilities governing monomer addition (and therefore the reactivity ratios) must be

independent of solvent, and that the role of the solvent is to influence the relative concentrations of monomers available to the growing chain end. Harwood has provided convincing evidence for this behavior in the copolymerizations of styrene with acrylic acid, methacrylic acid and acrylamide, and in the copolymerization of vinylidene chloride with methacrylonitrile.

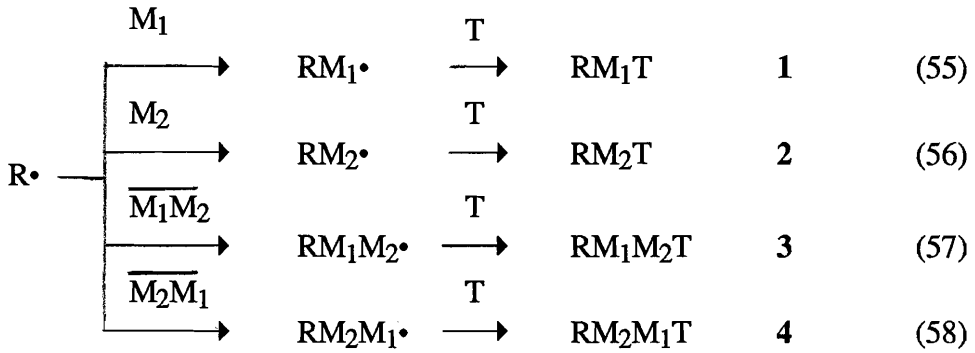
Measurements of Absolute Rate Constants. Each of the copolymerization models predicts not only composition and sequence, but also the overall propagation rate constant, k_p, as a function of monomer feed composition. Fukuda and coworkers[115] used a rotating sector technique to determine k_p over a range of feed compositions for the copolymerization of styrene and methyl methacrylate. They found large and systematic deviations from the predictions of the terminal model, but were able to reproduce their experimental observations by assuming a small penultimate effect. This is an intriguing observation in view of the "classic" nature of the styrene/methyl methacrylate copolymerization, and suggests that absolute rate measurements may prove particularly powerful in probing copolymerization mechanism.

Model Reactions. The mechanistic assumptions of the terminal, penultimate and complex participation models may be evaluated via trapping experiments with simple alkyl radicals. For example, the penultimate model, as applied to the copolymerization of monosubstituted olefins, implies that the selectivity of the attacking radical should be sensitive to the nature of the substituent that lies γ to the radical center:

$$\sim\sim\sim CH_2\underset{\gamma}{CH}CH_2\underset{\alpha}{CH}\bullet \qquad (54)$$

Tirrell and coworkers have determined the relative rates of addition of acrylonitrile and styrene (k_A/k_S) to a series of y-substituted propyl radicals,[131] and report that a y-cyano group depresses the relative affinity of the radical center for acrylonitrile by a factor of 3.5. This "penultimate effect" is remarkably consistent with those inferred by Hill and coworkers via composition and sequence analyses,[130] and lends support to the penultimate model as a physically realistic description of the copolymerization of styrene and acrylonitrile. Analogous measurements of k_A/k_S for the 1-phenylethyl[132] and 1-cyanoethyl[133] radicals are consistent with this view.

Trapping experiments have also been applied to the evaluation of the complex participation model. The hypothesis that olefinic EDA complexes add in concerted fashion to alkyl radicals - the fundamental assertion of the model - is subject to direct experimental test, as shown in Eqns 55-58.



The radical of interest, R•, is generated in the presence of M_1, M_2 and a radical trap (T). If R• undergoes concerted complex addition, trapping of the simple olefin adducts RM_1• and RM_2• will not be observed. Determination of the yields of products **1** and **2** then allows an estimate of the maximum extent to which the complex participates in the consumption of M_1 and M2. Jones and Tirrell have reported trapping experiments on the 1-butyl radical in its reactions with N-phenylmaleimide and two donor olefins (2-chloroethyl vinyl ether and styrene).[134,135] In each case, simple addition of N-phenylmaleimide was the dominant reaction; no evidence for concerted addition of the EDA complex was obtained.

Table I

Monomer Reactivity Ratios in Radical Copolymerization[a]

M_1	r_1	M_2	r_2	References
Acrylonitrile	0.030-0.100	Butadiene	0.10-0.45	10-14
	7.00	Ethylene	0.00	15
	6.00	Maleic Anhydride	0.00	16
	0.14	Methyl Methacrylate	1.32	17
	0.00-0.17	Styrene	0.29-0.55	18-27
	4.05-5.51	Vinyl Acetate	0.040-0.060	28,29
	2.55-4.00	Vinyl Chloride	0.020-0.070	30-34
Butadiene	0.50-0.75	Methyl Methacrylate	0.027-0.32	35-37
	1.35-1.83	Styrene	0.37-0.84	14,37-44
	8.80	Vinyl Chloride	0.04	45
Ethylene	0.40	Maleic Anhydride	0.00	46
	0.050	Styrene	14.9	47
	0.13-0.88	Vinyl Acetate	0.72-3.74	48-53
	0.020-0.34	Vinyl Chloride	0.96-4.38	54-62
Maleic Anhydride	0.010-0.020	Methyl Methacrylate	3.10-6.36	63-66
	0.000-0.020	Styrene	0.000-0.097	67-76
	0.40-0.67	Vinyl Chloride	0.040-0.100	77
Methyl Methacrylate	0.22-0.64	Styrene	0.28-0.62	78-97
	22.2-28.6	Vinyl Acetate	0.030-0.070	98-100
	8.99	Vinyl Chloride	0.070	101
Styrene	18.8-60.0	Vinyl Acetate	0.010-0.16	102-104
	12.4-25.0	Vinyl Chloride	0.005-0.160	32,105-108
Vinyl Acetate	0.24-0.98	Vinyl Chloride	1.03-2.30	101,102,109-113

[a]Values shown represent a range selected from a listing of reactivity ratios provided by R.Z. Greenley as a personal communication to the author.

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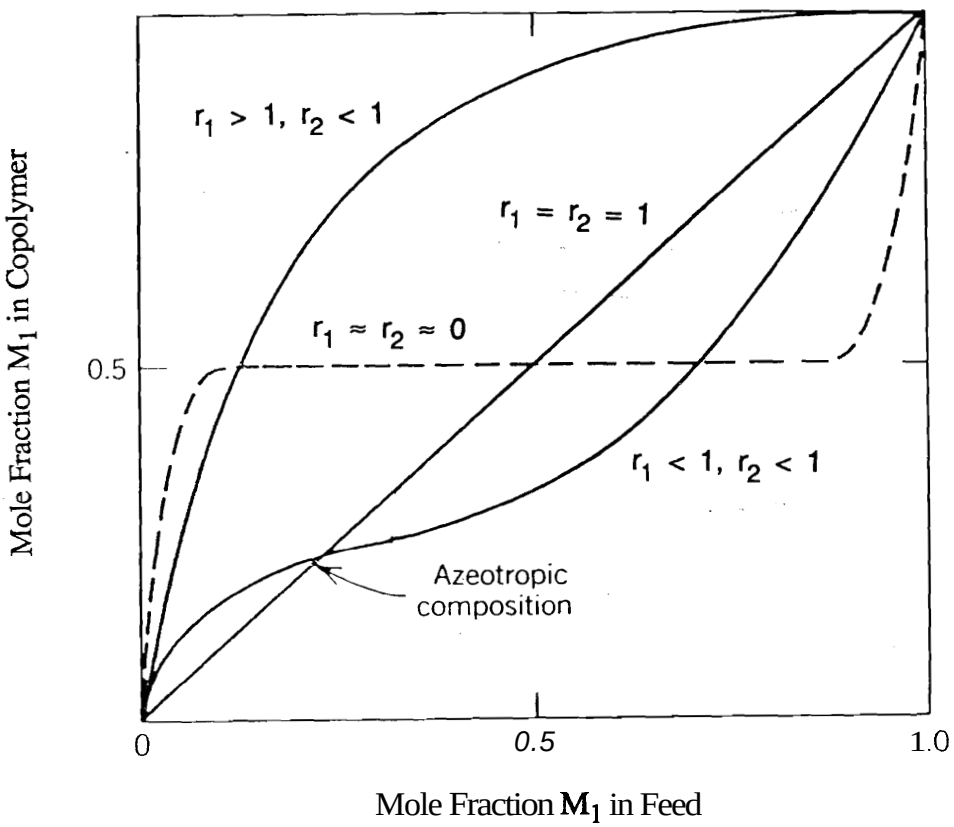
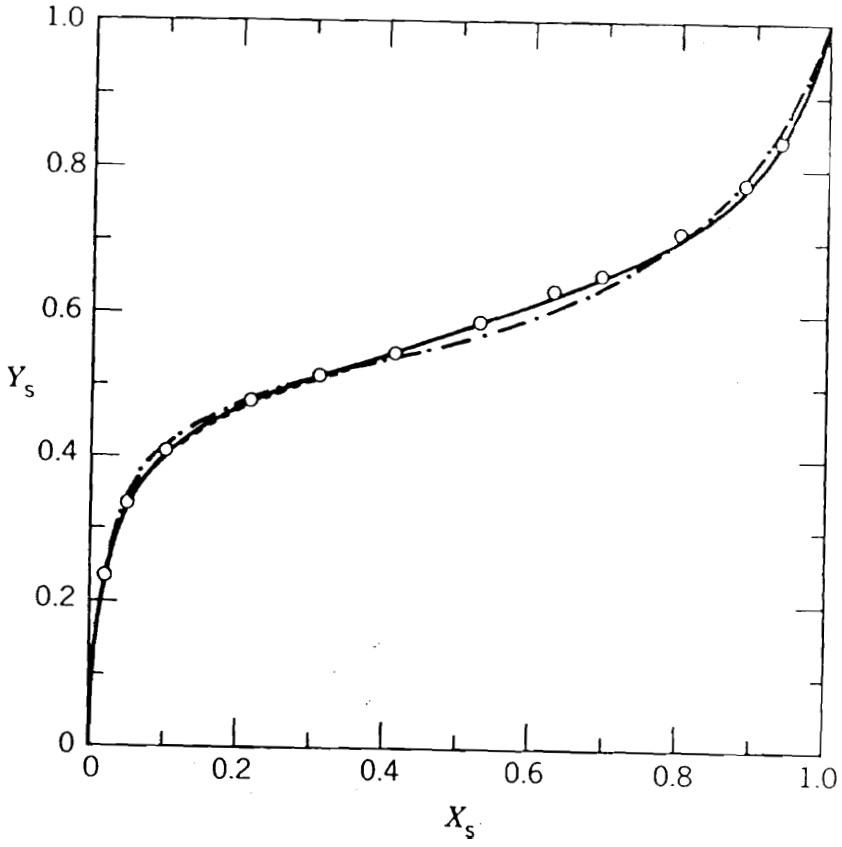
FIGURE CAPTIONS

Fig. 1. Copolymer composition (mole fraction M_1 in copolymer) as a function of monomer-feed composition (mole fraction M_1 in feed) for various reactivity ratio combinations.

Fig. 2. Copolymer composition curve for the copolymerization of acrylonitrile and styrene in bulk at 60°C. Y_S = mole fraction styrene in copolymer; X_S = mole fraction styrene in comonomer feed. O, experimental data; ——, penultimate model and complex model with no restriction; -----, complex model with equilibrium constant for complexation fixed at 0.52; — · — · —, terminal model. Reprinted with permission from ref. 114.

Fig. 3. Number fraction of styrene sequences of length 1 (N_{ASA}) in copolymers of acrylonitrile and styrene, as a function of the mole fraction of styrene in the monomer-feed mixture (X_S). O, experimental; ——, complex model with no restriction; -----, complex model with equilibrium constant for complexation fixed at 0.52; - - - -, penultimate model; — · — —, terminal model. Reprinted with permission from ref. 114.


$r_1 > 1, r_2 < 1$
$r_1 = r_2 = 1$
$r_1 \approx r_2 \approx 0$
$r_1 < 1, r_2 < 1$
Azeotropic composition
0.5
0
0.5
1.0
Mole Fraction M_1 in Copolymer
Mole Fraction M_1 in Feed


1.0
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Y_s
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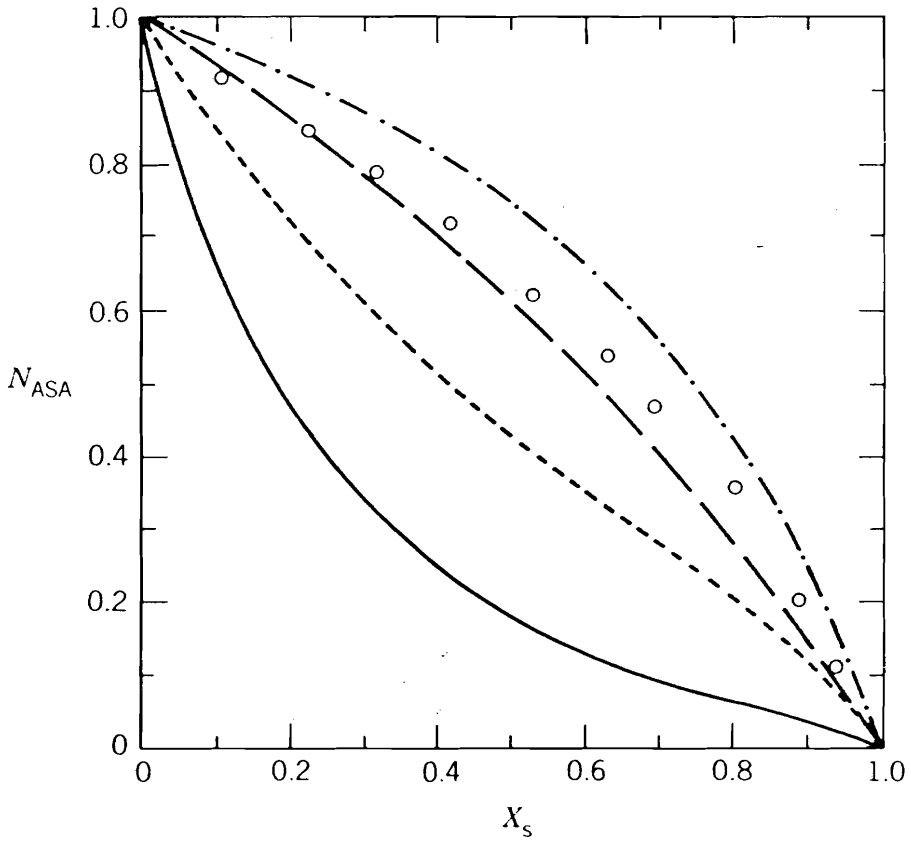
1.0
0.8
0.6
0.4
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0
N_{ASA}
0
0.2
0.4
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0.8
1.0
X_S